

CHARACTERIZATION AND ADSORPTION TREATMENT OF VACUUM RESIDUE FRACTIONS WITH CARBONS

Kinya Sakanishi, Toru Manabe, Izumi Watanabe, and Isao Mochida

Institute of Advanced Material Study, Kyushu University
Kasuga, Fukuoka 816-8580, Japan

Keywords: Vacuum residue fractions, step scan liquid mode XRD, adsorption treatments

ABSTRACT

The adsorption treatment of VR by using variable amounts of carbon particles was performed with stirring at 60 °C for 1 h. After the treatment, the adsorbent was first washed with n-hexane and then thoroughly washed with THF(tetrahydrofuran) under the ultrasonic irradiation to recover the soluble fractions of hexane soluble(HS) and hexane insoluble but THF soluble(HI-THFS) from the adsorbent. The THF insoluble(THFI) yield increased with the added amount of Ketjen Black(KB). The HI but THF soluble fraction decreased with the increased amount of THFI fraction. About 3 wt% of KB addition based on VR appeared enough for the selective removal of the heavier fraction without increasing the HI-THFS fractions. The slow step scan XRD revealed that the untreated KB showed a very slight peak around 26°. The adsorbed THFI exhibited a broad peak around 26°, while the relatively sharp peak of the original asphaltene around 26° decreased with the addition of KB, indicating selective adsorption of the heavier fraction in the asphaltene. Based on the above results, it is suggested that a certain amount of KB addition may selectively separate the heavier fraction, where the more polar and metal-containing compounds are concentrated, from the VR. Such an adsorption treatment using carbon nanoparticles is expected to remove the catalyst poisons such as the heavier asphaltene and metallic compounds prior to the catalytic upgrading hydrotreatments.

INTRODUCTION

It is desirable to remove metallic compounds in petroleum residues before catalytic hydrocracking and hydrodesulfurization reactions in refineries, because they cause severe catalyst deactivation.¹⁻³ They are usually concentrated in the asphaltene fraction which is known to be comprised of micellar aggregates.⁴ The micellar structure is believed to be formed through intermolecular aromatic plane stacking, hydrogen bonds, and charge transfer interactions. Such a micelle structure of the asphaltene interferes with its conversion into smaller molecules as it promotes the production of sludge and coke precursors over the catalyst through retrogressive reactions of dealkylation and dehydrogenative condensations, especially under the severe conditions used to achieve high conversions via hydrocracking.⁵⁻⁸

The metallic compounds in the asphaltene and/or polar fractions are deposited onto the catalyst along with a considerable amount of carbon precursors, and deactivate the hydrogenation activity. These deposits also enhance dehydrogenation reactions and coke formation in the hydrotreating processes. Hence, the deoagulation of the asphaltene fraction is very important for its depolymerization so as to allow the demetallation to proceed with minimal carbon deposition. There have been many reports on attempted ways to handle the asphaltene, such as extractive removal, solvation, and hydrogenation.⁹

In the present study, the aggregate structure of a vacuum residue and its fractions is investigated by step scan XRD at variable temperatures with or without solvent, in order to clarify the changes in

their micellular structure during the heating or the solvation. In addition, adsorptive concentration of the heavy asphaltene fraction from the vacuum residue by using carbon particles is also applied for the removal of catalytic poisons in the following catalytic upgrading processes.

EXPERIMENTAL

An Arabian mix crude vacuum residue (VR) was used in the present experiments. VR was fractionated by hexane extraction. In the present study, the hexane insoluble(HI) and soluble (HS) fractions were defined as asphaltene and maltene, respectively. The HS was further fractionated into three components of saturates(Sa), aromatics(Ar), and polars(Po) by a conventional alumina column chromatography. The elemental analyses of the fractions before and after the hexane fractionation are summarized in Table 1. Some properties of carbon supports used in the present study are summarized in Table 2.

The adsorption treatment of VR(20 g) by using variable amounts of carbon adsorbent(0 - 4.0 g) was performed with stirring at 60 °C for 1 h. After the treatment, the adsorbent was first washed with n-hexane and then thoroughly washed with THF(tetrahydrofuran) under the ultrasonic irradiation to recover the soluble fractions of hexane soluble(HS) and hexane insoluble but THF soluble(HI-THFS) from the adsorbent. The yield of the THF insoluble residue was calculated based on the weight of the dried adsorbent.

The step scan XRD(a high resolution liquid mode by Rigaku-2000) of VR fractions was measured by the scan speed of 0.4 sec/0.01 ° at variable temperatures of 30 to 300 °C with or without solvent of toluene of variable amounts.

RESULTS AND DISCUSSION

Composition and Structure of VR Fractions

The VR was consisted of 7.4 % HI and 92.6 % of HS, the latter of which was further fractionated into 16.3 % of Sa, 50.2 % of Ar, and 26.1 % of Po. The heteroatom-containing compounds including metallic compounds were concentrated in the HI as summarized in Table 1.

The XRD patterns of VR fractions are shown in Figure 1. The original VR showed a broad peak around 20 ° with a rather sharp shoulder peaks around 22 ° and 24 °. The HI showed a relatively sharp peak around 26 ° with a slight peak of 20 °, reflecting their larger aromatic rings and their stacking aggregate structure. Ar and Sa showed a rather sharp peak around 20 °, indicating entanglement of their longer alkyl chains of variety and polymethylene entanglement. The Po fraction showed a similar peak around 26 ° to that of the HI with a higher peak around 20 °, suggesting the similar structure to the asphaltene but with a smaller aromatic ring and molecular weight, and longer alkyl chains as reported in a previous paper.⁹

The Effect of the Heating and Solvent on the Aggregate Structure of the Asphaltene

Figure 2 shows the XRD patterns of VR during the heating from 30 to 300 °C. The sharp peaks around 22 and 24 ° disappeared by the heating to 100 °C, and the broad peak around 20 ° was shifted to the smaller angle direction during the heating up to 300 °C, suggesting that the aliphatic chain entanglement may be liberated by the heating. The shoulder peak around 26 ° derived from the asphaltene fraction also disappeared by the heating up to 200 °C. Figure 3 shows the XRD pattern of HI during the heating to 300 °C. The peak around 26 ° was not changed by the heating to 200 °C, while the further heating to 300 °C weakened the peak very much, but it was still survived at a high temperature 300 °C in the case of the asphaltene fraction alone.

10 to 30 % addition of toluene to VR decreased the peaks around 22 ° and 24 ° with the broadening of the peak around 20 °. These peaks were almost completely removed by the addition of 50 % toluene. On the other hand, the addition of toluene to the HI broadened the whole peak with decreasing markedly the peak of 26 °. The larger amount of toluene addition over 75 % appeared necessary for the complete removal of the peak around 26 ° derived from aromatic plane stacking.

Adsorption Treatment of VR by Carbon Supports

Figure 4 shows the yields in the adsorption treatment of VR by KB at 60 °C. The THF insoluble(THFI) yield increased with the added amount of KB, and 2.0 g of KB addition removed almost completely the HI fraction from VR as THFI. The HI but THF soluble fraction decreased with the increased amount of THFI fraction. 0.6 to 1.0 g of KB addition appeared enough for the selective removal of the heavier fraction without increasing the HI-THFS fractions. Figure 5 illustrates the XRD profiles of the THFI before and after the adsorption treatment by KB. The untreated KB showed a very slight peak around 26°. The adsorbed THFI exhibited a broad peak around 26 °, while the relatively sharp peak of the original asphaltene around 26 ° decreased with the addition of KB, indicating selective adsorption of the heavier fraction in the asphaltene.

Figure 6 illustrates the comparison of the adsorption treatments of VR with variable carbon adsorbents. The heavier fraction in VR was selectively adsorbed on carbon blacks and mesoporous carbons, but never adsorbed onto the microporous activated carbon fibers such as OG-7A and 15A.

Table 2 also summarizes the adsorbed amount of THF insoluble(THFI) with the metal concentrations analyzed by XRF measurements. MA 600 adsorbed the very small amount of THFI (0.37 wt%) with the higher concentrations of V(489 ppm) and Ni(187 ppm), although its surface area was as low as 150 m²/g. Carbon blacks of KB-600JD and BP2000 were also effective for the removal of the concentrated heavy fraction from VR, although the adsorbed amount of THFI was relatively higher than the other carbon adsorbents. A efficient recovery procedure of the heavier fraction from carbon black particles of high surface area should be designed for the application of such adsorbent to the upgrading of VR.

Based on the present study, mesoporous carbon particles can be a candidate for the selective removal of metal-containing heavy asphaltene fraction from VR and the regenerative recovery without too strong adsorption of the polar and heavier fraction.

ACKNOWLEDGMENT

This work has been carried out as a research project of The Japan Petroleum Institute commissioned by the Petroleum Energy Center with the subsidy of the Ministry of International Trade and Industry.

REFERENCES

1. Speight, J.G. *"The Desulfurization of Heavy Oils and Residua"*, Dekker, New York, 1981.
2. Nelson, W.L. *Oil & Gas J.* **1976**, 74, 72.
3. H.R.Siewert, H.R.; Koenig, A.H.; Ring, T.A. *Hydrocarbon Process.* **1985**, 64, 61.
4. Yen, T.F.; Erdman, J.G.; Pollack, S.S. *Anal.Chem.* **1961**, 33, 1587.
5. Howell, R.L.; Hung, C.W.; Gibson, K.R.; Chen, H.C. *Oil & Gas J.* **1985**, 83, 121.
6. Mochida, I.; Zhao, X.Z.; Sakanishi, K.; Yamamoto, S.; Takashima, H.; Uemura, S. *Ind. Eng. Chem. Res.*, **1989**, 28, 418.
7. Mochida, I.; Zhao, X.Z.; Sakanishi, K. *Ind.Eng.Che.Res.*, **1990**, 29 334.
8. Sakanishi, K.; Zhao, X.Z.; Mochida, I. *J. Petrol. Inst. Jpn.* **1992**, 35, 203.
9. Sakanishi, K.; Yamashita, N.; Whitehurst, D.D.; Mochida, I. *Catal. Today*, **1998**, 43, 241.

Table 1 Elemental Analysis of Arabian mixed crude vacuum residue

Sample	Carbon (wt%)	wt%				H/C	N/C	Vanadium (ppm)
		C	H	N	Others			
Original VR	100.0	84.4	10.4	0.19	4.9	1.48	0.003	87
HS	92.6	84.5	10.8	0.24	4.4	1.53	0.002	90
Sa	16.3	85.6	13.3	0.04	0.74	1.85	0.000	-
Ar	50.1	84.3	10.2	0.30	5.4	1.45	0.002	-
Po	36.1	82.6	8.6	0.83	8.1	1.24	0.009	-
HI	7.4	84.1	7.4	0.82	7.6	1.06	0.008	998

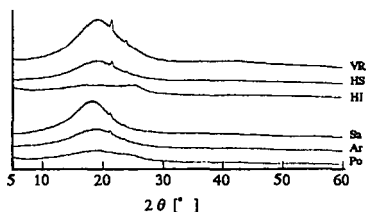


Figure 1 XRD of each Fraction in VR (Step Scan 4sec/0.01°)

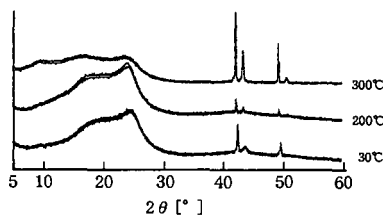


Figure 3 XRD of Heated HI (Measuring Temp. 30 to 300°C, Step Scan 4sec/0.01°)

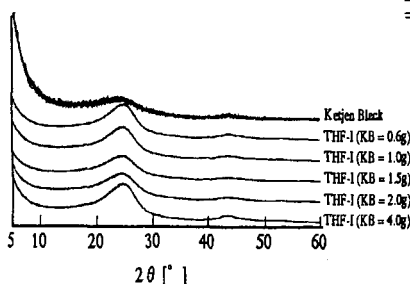


Figure 5 XRD of THFI adsorbed on KB (VR/KB = 20.0g/Xg, Mixing Time = 1h, Temp = 60°C, Step Scan 4sec/0.01°)

Table 2 Some properties of carbon adsorbents and their adsorption performance of VR

	S.A. [m ² /g]	ave. radius (Å)	adsorbed as THF-I [wt %]	V of adsorbed fraction [ppm]	Ni of adsorbed fraction [ppm]
KB 600JD	1270	-	1.42	301	128
MA600	150	-	0.37	489	187
BP2000	1475	-	2.00	256	132
OG-7A	957	8.36	0.00	-	-
OG-15A	1776	9.76	0.00	-	-
OG-20A	1930	9.83	0.10	61	192
MP-60	1276	16.50	0.78	188	70
MP-90	1371	21.10	1.62	200	69

Initial HI : V = 239ppm, Ni = 108ppm
Unadsorbed HI onto 0.6g of KB : V = 214ppm, Ni = 83ppm

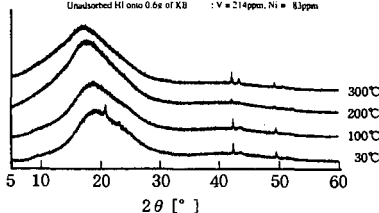


Figure 2 XRD of Heated VR (Measuring Temp. 30 to 300°C, Step Scan 4sec/0.01°)

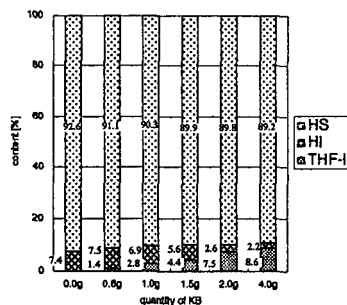
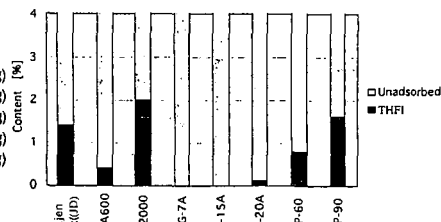


Figure 4 Adsorption of VR into KB (VR/KB = 20.0g/Xg, Mixing Time = 1h, Temp = 60°C)



(VR = 20.0g, Carbon = 0.6g, Mixing Time 1h, Temp 60°C)

Figure 6 Adsorption treatment of VR with variable carbons